Eastern Regional Research Laboratory
Philadelphia 18, Pennsylvania

PREPARATION OF RUTIN FROM BUCKWHEAT LEAF MEAL AND GREEN BUCKWHEAT WITH HOT SOLVENTS

J. F. Couch, C. F. Krewson, and J. Naghski

Bureau of Agricultural and Industrial Chemistry
Agricultural Research Administration
United States Department of Agriculture

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I. INTRODUCTION

Processes previously described for preparing rutin from buckwheat include cold solvent extraction of green buckwheat[1] and buckwheat leaf meal[2], and hot water extraction of buckwheat leaf meal[2]. For a general description of the chemistry and therapeutic use of rutin, the reader is referred to AIC-115[3].

The present circular describes an improved process based on extraction with hot dilute isopropyl alcohol, and includes specific directions for successful operation on a manufacturing scale. The procedure is applicable to either the green or dried plant with only minor changes in details. The hot solvent process has certain advantages over some of the older processes. The extraction is accomplished much more quickly, the solvent is removed from the extract more rapidly, and there is no necessity for rectification of the recovered solvent, since it distills at a strength high enough to permit its re-use in the process. In many cases the distillate is too strong for this purpose and requires dilution before being added to a new batch. This is especially true when dried plant (buckwheat leaf meal) is being processed.

The recommended procedure has been thoroughly tested in a number of runs. Tartary buckwheat was used because of the superiority of this species for rutin production and because most manufacturers are now utilizing it in preference to the Japanese, which is the more common variety and the one used for the production of grain and buckwheat pancake flour.

The various steps in the process are presented in a series of numbered directions. Detailed information and explanatory statements regarding the various steps appear in italics.

[1] J. F. Couch, C. F. Krewson, and J. Naghski. Extraction and Refining of Rutin From Green Buckwheat. Eastern Regional Research Laboratory. AIC 160. July 1947.

[2] R. K. Eskew, G. W. Macpherson Phillips, Edward L. Griffin, Jr., A. Shaines and Nicholas C. Aceto. Production of Rutin from Buckwheat Leaf Meal. Eastern Regional Research Laboratory. AIC 114. Revision 1 June 1948.

[3] J. F. Couch, C. F. Krewson, J. Naghski, and M. J. Copley. The Chemistry and Therapeutic Use of Rutin. Eastern Regional Research Laboratory. AIC 115. April 1946.

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II. EXTRACTION

1. Select a steam-heated extractor (or extractors) of suitable size made of stainless steel, wood, or glass; avoid iron, copper, or aluminum equipment.

The same style extractor may be used for either green plant or meal extraction. It may vary in size, shape, construction material, and heating unit, depending on equipment available and magnitude of operations planned. For production of an equal quantity of rutin, extractor capacity required for green buckwheat may be several times that required for the extraction of leaf meal. The extractor should be tightly covered, and if the marc is to be stripped of solvent in this container, it should be equipped with a condenser. A condenser will also prevent loss of solvent during heating. If a wooden extractor is used, the solvent may be preheated by a heat exchanger; the extraction is then carried out effectively at slightly lower than the boiling point of the solvent. A countercurrent extraction system or some form of continuous hot extraction should be equally effective.

In extracting green buckwheat, no provision need be made for screening or filtering the extracts, since whole plant (less roots) is usually packed into the extractor without cutting. To facilitate packing and unloading the extractor, however, the green plant may be cut into about 2-inch pieces, but mincing or crushing should be avoided. In extracting buckwheat meal, provision must be made to filter the marc from the extracts when the latter are withdrawn for evaporation. This may be accomplished by a filter press in the line or, more simply, by a false bottom in the extractor if a tank-type extractor is selected. The bottom of the extractor is covered with a 4- to 6-inch layer of excelsior, over which a layer of cheesecloth is placed and tucked in around the edges to hold it in place. The false bottom is anchored by the dry meal before addition of solvent. The hot solvent penetrates the plant rapidly and thoroughly without mechanical agitation. If the false bottom is made of fine stainless steel screen, the bed of buckwheat meal serves as its own filtering medium when the extract is sufficiently recirculated from bottom to top of the extractor.

2. Fill the extractor to a convenient level with dilute isopropyl alcohol and green buckwheat or buckwheat leaf meal.

The green plant is packed at the ratio of 150 to 200 pounds to the 100-gallon extractor, with 60 to 75 gallons of 80- to 85-percent (by volume) of isopropyl alcohol. The yield of rutin diminishes appreciably if isopropyl alcohol greater than 85 percent strength is used.

The meal (either whole plant meal or leaf meal) is packed at the ratio of 60 pounds to the 100-gallon extractor, with 90 gallons of 70- to 85-percent (by volume) of isopropyl alcohol. Stronger or weaker isopropyl alcohol should be avoided, since the yields of rutin fall off appreciably with strengths above and below these limits. With isopropyl alcohol of lower strength, emulsion difficulties occur, and rutin does not crystallize completely. Also, the quantity of the so-called "alcohol-insoluble" material appearing as an impurity in crude rutin is reduced if 85-percent isopropyl alcohol is used.

3. Bring the solvent to a boil and hold at the boiling temperature for 10 minutes.

In extracting green plant, heating for periods longer than 10 minutes should be avoided. The yield of rutin is decreased when the heating time is increased. When buckwheat leaf meal is used, the heating time is much less critical. Experimental data from extraction of buckwheat leaf meal show that the yield of rutin was identical when 10-minute and 2-hour boiling periods were used. The data also show that periods of boiling longer than 2 hours give diminishing returns. A 12-percent loss of rutin was experienced with a 14-hour heating.

4. Draw off the extract; filter if necessary.

Under no circumstances should plant material be permitted to enter the evaporator along with the extract. If screening has not been adequate during removal of extract and wash liquors, the rutin solution should be filtered before it is transferred to the evaporator.

5. Cover the marc with fresh dilute solvent, heat the contents of the extractor to boiling, and draw off the wash liquor, filtering if necessary.

For green plant, 35 to 40 gallons of 80- to 85-percent isopropyl alcohol per 150 to 200 pounds of plant is sufficient for this operation. For buckwheat meal, 35 gallons of 70- to 85-percent isopropyl alcohol per 60 pounds of meal is sufficient.

6. Wash the marc again with hot solvent.

The quantities of solvent used for the second washing are identical with those used for the first washing. The procedure described will extract 96 to 99 percent of the rutin present in a buckwheat leaf meal. If quantitative recovery is desired, additional washings may be made. The solution from the second washing may be used to make the first washing of new plant, or as previously mentioned, some form of countercurrent system may be set up for the extraction. With gravity drainage, there is appreciable hold up of isopropyl alcohol in the marc. The solvent may be completely removed by stripping or partially removed by washing with water followed by rectification. Appreciable quantities of the entrained alcohol may be removed by pressure if the extractor is of suitable construction, or by use of a continuous vacuum filter press. The possibility of using a rotary filter press as a substitute for the washing carried out in steps 5 and 6 has not been investigated.

7. Distill off the solvent completely from the combined extract and washings.

This requires about a 90-percent reduction in volume. Vacuum is not necessary for this evaporation. If vacuum is applied, the temperature of the mixture after removal of solvent will be less than that of boiling water at atmospheric pressure, and the rutin will not remain in solution. In this case, sufficient water will have to be added to redissolve the rutin before proceeding. Often this requires a large quantity of water. If no vacuum is used, the rutin will remain in solution.

8. To the boiling concentrate, add 2 to 3 volumes of boiling water and continue boiling for about 15 minutes.

The quantity of boiling water added should be sufficient to bring the rutin concentration to approximately 1 pound per 20 to 30 gallons of water.

9. Draw off the boiling concentrate from the evaporator to a steam-jacketed holding tank, straining the fats through a glass-wool filter mat.

The dilution mentioned in step 8 may also be made in the holding tank, if this procedure is more convenient. The fats would then be strained off before dilution, provided rutin has not precipitated. Dilution at this stage is not critical; as much as 40 gallons and as little as 15 gallons of water per pound of rutin have been used without apparent differences in quality and yield of rutin. The bulk of the fats is removed[4] from the boiling concentrate by straining through glass wool or similar material, thus taking the load off the filter press and rendering the subsequent filtration more efficient. A convenient strainer is constructed of 1/4- to 1/2-inch mesh galvanized wire (hardware cloth). In bending the wire to make the box described in AIC-160, it should be folded up so that the sides are also formed of the same material. This construction gives added strainer capacity.

10. Filter the boiling, strained liquid through heavy filter sheets backed with canvas.

An area of 2 to 3 square feet is required for each pound of rutin or about 10 to 15 square feet per 100 gallons of rutin solution. High "polish" is desired in this filtration operation, in order to remove fat mechanically and to remove colloidal impurities by adsorption. The filter sheets should be paper of fine porosity grade. Those manufactured by the Republic Seitz Filter Corporation[5] have proved satisfactory. Sheets K-5 and S-1 have been used at this stage. Paper similar to Sheet S-3, the finest grade serum paper, has been used for filtration in the recrystallization stages. The flow rate for these sheets is considerably increased when they are backed by canvas. Small quantities of filter aid such as diatomaceous silica (the fine porosity grades) renders the filtration more efficient. Some commercial filter aids tested have interfered with recovery of rutin. Other filter aids or adsorbents may prove more effective, but this field has not been thoroughly investigated. These materials should always be tested before use to make certain that they contain no free alkali. In the filtration operations of rutin manufacture and refining, not more than 10 pounds of pressure per square inch should be allowed to develop on a filter press. If pressure is allowed to develop in the filtration of fat, the fat will be pushed through the filtering medium. Inspect the outlet side of the filter sheets to see that this has not occurred.

11. Cool the rutin filtrate.

The cooling tanks should be jacketed or equipped with cooling coils and supplied with some means of mechanical stirring. Wooden tanks are not satisfactory for this operation, because they cannot be kept sterile. Rapid cooling to low temperature is desirable. Cooling by running water and good agitation is usually achieved in less than an hour.

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4 FURTHER DETAILS ARE DESCRIBED IN AIC-160.

5 THE MENTION OF COMMERCIAL PRODUCTS DOES NOT IMPLY THAT THEY ARE ENDORSED OR RECOMMENDED BY THE DEPARTMENT OF AGRICULTURE OVER OTHERS OF A SIMILAR NATURE NOT MENTIONED.

12. Allow the cooled rutin filtrate to stand for 2 hours at low temperature.

If rutin solutions saturated at the boiling temperature are cooled to 40 - 50° F., the rutin will crystallize completely in 2 hours. If desired, crushed ice may be added to the rutin solutions after they have been cooled with cold water.

CAUTION: *The ice should be free of iron and alkali. The rutin solutions should not be held longer than 24 hours at room temperature; otherwise, fermentation may occur.*

13. Filter off the crude rutin on a filter press, using a hard-surface paper (sharkskin or rayon fiber) or heavy canvas. Wash the crystals with cold water.

It is most desirable to reserve a separate filter press for this operation. The press used for removal of fats should not be used for the crude rutin filtration, since it is almost impossible to clean thoroughly and remove traces of fat from the valves and fittings of the equipment.

14. Remove the crude rutin from the filter press and slurry it with a small quantity of cold water. Filter and air-dry.

If the rutin is to be stored, dry at 220° F. If it is to be recrystallized within 24 hours, it may be stored wet in a cold room.

III. REFINING

(A) RECRYSTALLIZATION FROM WATER

15. Dissolve the crude rutin in boiling water with mechanical agitation.

If the rutin has been dried, it should be powdered to facilitate solution. Use about 20 gallons (cold measurement) of water to each pound of crude rutin. If the rutin has not been dried, it will usually contain approximately 40 to 50 percent moisture. In either case, use sufficient boiling water to dissolve the rutin completely. If tap water is used it must be tested to make sure it is free of alkali. The water should be boiled for 10 minutes, after which the pH should not exceed 6.5. If necessary, adjust with sulfuric acid before using. In alkaline solution or strongly acid solution (pH less than 1.5), rutin is rapidly hydrolyzed.

16. Boil the crude rutin solution for 15 to 20 minutes to agglomerate colloidal material.

17. Filter the boiling solution through heavy filter sheets backed with canvas.

One to two square feet of filtering area for each pound of crude rutin processed is adequate. Hot water insoluble impurities should be removed at this point to prevent fouling the silica gel in the subsequent step. A small quantity of filter aid facilitates this operation.

18. To the boiling filtrate, add silica gel with rapid stirring. Boil for 10 minutes, continuing the agitation.

About one-half pound of silica gel (14 to 20 mesh) per pound of rutin processed is required. The silica gel removes so-called "red pigment." The quantity of "red pigment" in the rutin solution depends entirely on the efficiency (degree of polishing) achieved in the previous filtering operations. With extreme efficiency in the previous filtration, the quantity of silica gel may be reduced, or it may even be eliminated. On the other hand, poor filtration at that stage may make it necessary to increase the quantity of silica gel used here. Filter sheets of the type recommended contain asbestos, which aids in removing "red pigment." The need for good filtration facilities in rutin manufacture and refining cannot be overemphasized.

19. After the treatment with the silica gel, filter the rutin solution through clean heavy filter sheets backed with canvas.

20. Cool the rutin solution, filter and wash as in steps 11, 12, and 13. Dry to constant weight at 220° F.

If the crude rutin is properly prepared and the filtrations are adequate at all stages, the refined rutin may be sufficiently free of extraneous material to render it of pharmaceutical purity; otherwise, removal of alcohol-insoluble material will be necessary.

(B) REMOVAL OF ALCOHOL-INSOLUBLE MATERIAL
(SEE SECTION (C) FOR ALTERNATE PLAN)

21. Dissolve thoroughly dried powdered rutin in boiling isopropyl alcohol (98 to 99 percent) at the rate of 1 pound per 1-3/4 gallons of solvent (solvent measured cold).

Moisture decreases the solubility of rutin in anhydrous alcohol. To insure complete solution at the rates specified, rutin should be redried after powdering and either used immediately or stored protected from the moisture of the atmosphere. Anhydrous ethyl and methyl alcohols are less satisfactory than isopropyl alcohol for removing alcohol-insoluble materials. If ethyl alcohol is used as a substitute for isopropyl alcohol, rutin is dissolved at the rate of about 1 pound to each gallon of solvent.

22. Concentrate the isopropyl alcohol solution to half volume. Cool to room temperature. Filter off insoluble material, using heavy asbestos sheets. Wash with small portions of cold isopropyl alcohol.

More extraneous material is removed by cooling the isopropyl alcohol solution before filtration than by filtering the hot solution. However, methyl or ethyl alcohol solutions should be filtered hot through heavy asbestos sheets. If cold filtration of methyl or ethyl alcohol solutions is attempted, rutin is likely to precipitate before filtration is completed.

23. Pour the filtrate and washings into 10 volumes of cold water.

The isopropyl alcohol may be recovered from the mother liquors after removal of the crystallized rutin, or the mother liquors may be used to adjust the strength of the solvent for the extraction operation.

If desired, the isopropyl alcohol solution may be poured into hot water and the isopropyl alcohol boiled off through a condenser.

24. Allow the solution to stand in the cold for about 24 hours for rutin to crystallize. Filter. Dry at 220°F.

(C) ALTERNATE PLAN FOR REMOVAL OF ALCOHOL-INSOLUBLE MATERIAL

Small-scale laboratory experiments have indicated that it is feasible to carry out the alcohol-insoluble removal without drying the rutin at step 20.

25. Place the wet rutin of step 20 (moisture content, 50 percent) in hot, 98- to 99-percent isopropyl alcohol in the ratio of 1 pound to 2 gallons of solvent. Distill, collecting 1.4 gallons of distillate for every 2 gallons of solvent used.

26. To the rutin solution, add a quantity of 98- to 99 percent isopropyl alcohol equal to that distilled in step 25. Continue distillation, collecting an additional 1.4 gallons of distillate for every 2 gallons of original solvent used. Rutin should be completely dissolved before the end of this operation.

27. Cool the rutin solution to room temperature, filter, and wash the filter cake with cold isopropyl alcohol.

28. Pour the filtrate and washings into 10 volumes of cold water and recover the rutin as previously described in steps 23 and 24.